

AIR QUALITY MONITORING CONSIDERATIONS FOR THE GREAT LAKES NETWORK PARKS

July 2003

Introduction

In FY 2002, the National Park Service (NPS) Air Resources Division (ARD) developed a strategy for expanding ARD-funded ambient air quality monitoring with increased funding from the Natural Resource Challenge. Based on that strategy, at this time, ARD does not intend to fund additional monitoring at any NPS units in the Great Lakes Inventory and Monitoring (I&M) Network. The ARD air monitoring strategy will be revisited in FY 2004 if additional funding becomes available.

Data from state, national and other air monitoring programs described below were used in conjunction with park-specific resource information to evaluate the following needs relative to the Great Lakes Network: 1) the need for additional ambient air quality monitoring at any Network park, *i.e.*, wet deposition, dry deposition, visibility, particulate matter, ozone and/or air toxics monitoring (rough cost estimates for installation and annual operation of some typical air quality monitoring stations are attached), and 2) the need for air quality effects-related monitoring at any Network park. The results of this evaluation, as well as a brief summary of results of current air quality monitoring at sites in the region, are discussed below.

Air Inventory

With funds from the National I&M Program, the ARD contracted with the University of Denver to develop baseline values for ozone, deposition and visibility for all I&M parks. The analysis involved interpolating concentrations between monitors to estimate pollutant values at parks that do not have on-site monitoring. The products include web-based GIS maps and tables for the parks. These products constitute the I&M Air Inventory. Air Inventory products are available at <http://www2.nature.nps.gov/ard/gas/> (see section called *Air Atlas*).

Deposition

Wet Deposition

The National Atmospheric Deposition Program/National Trends Network (NADP/NTN) is a nationwide network of precipitation monitoring sites (<http://nadp.sws.uiuc.edu>). The network is a cooperative effort between many different groups, including the U.S. Environmental Protection Agency (EPA), U.S. Geological Survey (USGS), U.S. Department of Agriculture, and private entities. The NPS is a major participant in NADP/NTN, and the ARD recommends that any new wet deposition site installed in a park meet NADP/NTN siting criteria and follow NADP/NTN protocols. There are currently more than 200 NADP/NTN sites spanning the continental U.S., Alaska, Puerto Rico, and the Virgin Islands.

The purpose of the network is to collect data on the chemistry of precipitation to monitor geographical and temporal long-term trends. The precipitation at each station is collected weekly according to strict clean-handling procedures. It is then sent to the Central Analytical Laboratory in Illinois where it is analyzed for hydrogen (acidity as pH), sulfate, nitrate, ammonium, chloride, and base cations (such as calcium, magnesium,

potassium and sodium). NADP/NTN's excellent quality assurance programs ensure that the data remain accurate and precise.

Deposition varies with the amount of annual on-site precipitation, and is useful because it gives an indication of the total annual pollutant loading at the site. Concentration is independent of precipitation amount, therefore, it provides a better indication of whether ambient pollutant levels are increasing or decreasing over the years. In general, annual average wet deposition and concentration of sulfate, nitrate, and ammonium are higher in the eastern than in the western U.S. (see attached Air Inventory wet deposition maps; also see NADP/NTN maps on their website). At many NADP/NTN sites across the U.S., concentration and deposition of sulfate have declined in recent years as sulfur dioxide emissions have decreased. Trends have been variable for nitrate and ammonium, with concentration and deposition at sites increasing, decreasing, or showing no overall change. These patterns are reflected in trend data from NADP/NTN sites in the Great Lakes region. Interestingly, a number of the regional sites show increases in pollutant deposition and concentration in the late 1990s. The cause of the increase is unknown. It's too early to tell if these data indicate a long-term increase in pollutant values. Results from NADP/NTN sites in the Great Lakes region are summarized below.

Indiana Dunes National Lakeshore, IN

Indiana Dunes National Lakeshore (NL), Indiana, has had a NADP/NTN site (site #IN34) since 1980. Wet concentration and deposition of sulfate have decreased at the site, while there has been no overall trend in wet concentration and deposition of nitrate and ammonium.

Chassell, MI

The NPS has operated an NADP/NTN monitor at Chassell, Michigan (site #MI99), about 60 miles southeast of Isle Royale National Park (NP), and 60 miles east of Apostle Islands NL, since 1983. Site data show wet sulfate concentration has decreased steadily since 1984, while wet sulfate deposition decreased through 1997, and then increased in 1998 through 2002. There has been no overall trend in wet concentration and deposition of nitrate and ammonium.

Isle Royale NP, MI

An NADP/NTN site was installed at Wallace Lake in Isle Royale NP, Michigan (site #MI97) in 1985. Because the site can't be accessed for winter sampling, data don't meet the completeness criteria required by NADP/NTN for a trend analysis.

Peshawbestown, MI

An NADP/NTN site was installed at Peshawbestown, Michigan (site #MI29) in 2002. This site is about 15 miles northeast of Sleeping Bear Dunes NL. Trend data are not yet available from the site.

Raco, MI

An NADP/NTN monitor has been operating at Raco, Michigan (site #MI98) since 1984. Site data show wet sulfate concentration and deposition decreased from 1985 to 1996, but there was no overall trend in wet concentration and deposition of nitrate and ammonium.

Since 1997, data have not met completeness criteria required by NADP/NTN for a trend analysis.

Seney National Wildlife Refuge, MI

An NADP/NTN site was installed at Seney National Wildlife Refuge (NWR), Michigan (site #MI48), about 25 miles southeast of Pictured Rocks NL, in 2000. Trend data are not yet available from the site.

Wellston, MI

An NADP/NTN monitor has been operating at Wellston, Michigan (site #MI53) since 1978. Site data show wet sulfate concentration and deposition have decreased steadily since 1979. Wet nitrate concentration has shown no overall trend, but wet nitrate deposition showed no trend through 1998, and then began to increase. Wet ammonium concentration and deposition showed no overall trend through 1998, and then began to increase.

Belle Prairie, MN

An NADP/NTN site has been operating at Belle Prairie, Minnesota (site #MN23 (Camp Riley)) since 1983. Site data show wet sulfate concentration and deposition have decreased slightly since 1985, with elevated values in 1998 and 1999. Wet nitrate and ammonium concentration and deposition have increased slightly since 1985, with elevated values in 1998 and 1999.

Cedar Creek, MN

An NADP/NTN site was installed at Cedar Creek, Minnesota (site #MN01) in 1996, approximately 25 miles northeast of the Mississippi National River and Recreation Area (NRRRA). Trend data are not yet available from the site.

Fernberg, MN

The NADP/NTN site at Fernberg, Minnesota (site #MN18 (Snowbank Lake)) has been operating since 1980. Wet sulfate concentration and deposition have decreased since 1982, with elevated values in 1998 and 1999. Wet nitrate concentration showed no overall trend, while wet nitrate deposition has decreased, with elevated values in 1998 and 1999. Wet ammonium concentration and deposition showed no overall trend, with elevated values in 1998 and 1999.

Fond du Lac, MN

An NADP/NTN site was installed at Fond du Lac, Minnesota (site #MN05) in 1996. This site is approximately 75 miles southwest of the Apostle Islands NL. Trend data are not yet available from the site.

Grindstone Lake, MN

An NADP/NTN site was installed at Grindstone Lake, Minnesota (site #MN28), about 25 miles southeast of the Saint Croix National Scenic River (NSR), in 1996. Trend data are not yet available from the site.

Hovland, MN

An NADP/NTN site was installed at Hovland, Minnesota (site #MN08) in 1996. This site is about 10 miles southwest of Grand Portage National Monument (NM). Trend data are not yet available from the site.

Marcell Experimental Forest, MN

The NADP/NTN site has been operating at Marcell Experimental Forest, Minnesota (site #MN16 (Balsam Lake)) since 1978. Wet sulfate concentration and deposition have decreased at the site since 1980, with elevated values in 1998 through 2000. There has been no overall trend in concentration and deposition of wet nitrate. Wet ammonium concentration and deposition have decrease slightly since 1980, with elevated values in 1998 through 2000.

Voyageurs NP, MN

An NADP/NTN site was installed at Voyageurs NP, Minnesota (site #MN32 (Sullivan Bay)) in 2000. Trend data are not yet available from the site.

Wolf Ridge, MN

An NADP/NTN site was installed at Wolf Ridge, Minnesota (site #MN99) in 1996. Trend data are not yet available from the site.

Lac Courte Oreilles Reservation, WI

An NADP/NTN site was installed at Lac Courte Oreilles Reservation, Wisconsin (site #WI97), approximately 70 miles south of the Apostle Islands NL in 2001. Trend data are not yet available from the site.

Spooner Lake, WI

An NADP/NTN monitor has been operating at Spooner Lake, Wisconsin (site #WI37), about 40 miles west of the Saint Croix NSR, since 1980. Site data show wet sulfate concentration decreased steadily through 1997, then leveled off, while wet sulfate deposition decreased through 1997, then began to increase. Wet nitrate concentration showed no overall trend through 1997, then began to increase, while wet nitrate deposition decreased through 1997, then began to increase. Wet ammonium concentration and deposition showed no overall trend through 1997, and then began to increase.

Trout Lake, WI

An NADP/NTN monitor has been operating at Trout Lake, Wisconsin (site #WI37), about 60 miles southeast of the Apostle Islands NL, since 1980. Site data show wet sulfate concentration generally decreased through 1995, then leveled off, while wet sulfate deposition decreased through 1997, then leveled off. Wet nitrate concentration has been steady since the early 1980s, while wet nitrate deposition decreased through 1986, then leveled off. Wet ammonium deposition shows no overall trend, and wet ammonium concentration has been steady except for a dip in concentrations in the late 1980s.

Dry Deposition

The Clean Air Status and Trends Network (CASTNet) is the nation's primary source for atmospheric data to estimate dry acidic deposition (<http://www.epa.gov/castnet>). Established in 1987, CASTNet now comprises over 70 monitoring stations across the U.S. The majority of the monitoring stations are operated by EPA; however, approximately 20 stations are operated by the NPS in cooperation with EPA. Each CASTNet dry deposition station measures weekly average atmospheric concentrations of sulfate, nitrate, ammonium, sulfur dioxide, and nitric acid; hourly concentrations of ambient ozone; and meteorological conditions required for calculating dry deposition rates. Dry deposition rates are calculated using atmospheric concentrations, meteorological data, and information on land use, vegetation, and surface conditions. CASTNet complements the database compiled by NADP/NTN. Because of the interdependence of wet and dry deposition, NADP/NTN wet deposition data are collected at or near all CASTNet sites. Together, these two long-term databases provide the necessary data to estimate trends and spatial patterns in total atmospheric deposition. The ARD recommends that all new dry deposition sites installed in parks use CASTNet siting criteria and follow CASTNet protocols.

Because CASTNet uses different monitoring and reporting techniques than NADP/NTN, the dry deposition amounts are reported here as nitrogen and sulfur, rather than nitrate, ammonium, and sulfate. In addition, because CASTNet calculates dry deposition based on measured ambient concentrations and estimated deposition velocities, there is greater uncertainty in the reported values. Due to the small number of CASTNet sites nationwide, use of dry deposition isopleth maps is not advised at this time. CASTNet data collected at sites in the Great Lakes region are summarized below.

Salamonie Reservoir, IN

The Salamonie Reservoir, Indiana, CASTNet site (site #SAL133) has been in operation since 1989. It is located 95 miles southeast of Indiana Dunes NL. There has been a decrease in dry sulfur deposition at the site, but no trend in dry nitrogen deposition. Total nitrogen deposition at the site is composed of 27 percent dry deposition and 73 percent wet deposition, while total sulfur deposition is 35 percent dry and 65 percent wet.

Hoxeyville, MI

A CASTNet monitor was installed in Hoxeyville, Michigan (site #HOX149) in 2000. This site is located about 45 miles southeast of Sleeping Bear Dunes NL and about 165 miles south-southeast of Pictured Rocks NL. Data are not yet available from the site.

Voyageurs NP, MN

A CASTNet site has been operating at Voyageurs NP, Minnesota (site #VOY413) since 1996. This site is about 110 miles west of Grand Portage NM, 130 miles west of Isle Royale NP, and about 130 miles northwest of the Apostle Islands NL. A trend analysis is not available for the site. Total nitrogen and sulfur deposition at the park are estimated to be 14 percent dry and 86 percent wet deposition.

Perkinstown, WI

A CASTNet site has been operating in Perkinstown, Wisconsin (site #PRK134) since 1989. This site is approximately 70 miles east of the Saint Croix NSR, 110 miles south of the Apostle Islands NL, and about 115 miles east of the Mississippi NRR. Data show a

decrease in dry sulfur deposition, but no trend in dry nitrogen deposition. Total nitrogen deposition at the site is estimated to be 18 percent dry and 82 percent wet, while total sulfur deposition is 23 percent dry and 77 percent wet.

Surface Water Chemistry

The NPS Water Resources Division's *Baseline Water Quality Data Inventory and Analysis* reports were reviewed for all nine Great Lakes Network parks. Air pollution concerns relative to surface water chemistry include acidification due to sulfur and nitrogen deposition, eutrophication from nitrogen deposition, and deposition of toxic air pollutants such as mercury, other metals, and organics. In general, acid-sensitive surface waters have a pH below 6.0 and an acid neutralizing capacity (ANC) below 100 microequivalents per liter ($\mu\text{eq/l}$). Small lakes, streams, ponds, and creeks are more likely to be sensitive to atmospheric deposition, while large lakes and rivers are typically not affected. Results for the Network parks are summarized below.

Apostle Islands NL

The 1999 *Baseline Water Quality Data Inventory and Analysis report* for Apostle Islands NL contains water chemistry data for lagoons and streams on Outer, Michigan, Stockton, and Oak Islands. The lagoon on Michigan Island appears to be well buffered, with average pH values of 6.3 to 6.6 and a minimum ANC of 200 $\mu\text{eq/l}$. Data from Oak Island Stream were quite variable, with pH values ranging from 5.5 to 7.3 and ANC values ranging from 88 to 520 $\mu\text{eq/l}$. Unfortunately, all data were collected at Oak Island in 1983 and 1984, and most were from single point measurements. Data from Stockton Island Stream and Lagoon were also variable, with average pH values ranging from 5.6 to 6.6 (minimum of 4.7) and ANC values ranging from 32 to 120 $\mu\text{eq/l}$. The most recent ANC data available for Stockton Island were collected in 1984. Data indicate the lagoon on Outer Island is sensitive to acidification from atmospheric deposition. Average pH values ranged from 5.6 to 6.3 (minimum of 4.9) and average ANC values ranged from 38 to 45 $\mu\text{eq/l}$ (minimum of 32 $\mu\text{eq/l}$).

Grand Portage NM

The 1999 *Baseline Water Quality Data Inventory and Analysis report* for Grand Portage NM shows limited data were collected in the park at Grand Portage and Poplar Creeks in 1995. The average pH was about 7.2, and the average ANC was about 500 $\mu\text{eq/l}$. These data indicate creeks in the monument are not sensitive to acid deposition.

Indiana Dunes NL

The 1994 *Baseline Water Quality Data Inventory and Analysis report* for Indiana Dunes NL shows water samples were collected from Pinhook and Cowles Bogs in the late 1970s. The bogs had an average pH of about 7.1 and an average ANC of about 1500 $\mu\text{eq/l}$. Data were collected in the Drive Point Dune Acres and Interdunal Ponds in 1977 and 1978. A couple of the dunes (D6 and D7) had comparable pH values but low ANC values relative to the rest of the dunes and the ponds, *i.e.*, average pH value of 7.0; ANC values of 100 $\mu\text{eq/l}$ versus 450 $\mu\text{eq/l}$. The Little Calumet River, Kintzele Ditch, and East Derby Ditch Tributary had average pH values around 7.0 and average ANC values around 1200 $\mu\text{eq/l}$. These data indicate park surface waters are not sensitive to acidification from atmospheric deposition. However, the occurrence of elevated levels of nitrogen compounds in some samples indicates eutrophication may be a concern. Given

the proximity of the park to urban areas, it may be difficult to determine if the primary mechanism for pollutants entering the park is via the air or the water. Most data contained in the report were collected prior to 1981 so it's unknown if these data are representative of current conditions in the park.

Isle Royale NP

The 1995 *Baseline Water Quality Data Inventory and Analysis report* for Isle Royale NP indicates water samples collected in 1984 from Lake Theresa and an unnamed lake had pH values of 7.0 to 7.9 and ANC values of 224 to 1021 $\mu\text{eq/l}$. Multiple sampling of Washington Creek between 1965 and 1993 provided average pH values of 7.4 and average ANC values of 464 $\mu\text{eq/l}$. Water samples collected in 1992 on a number of creeks and tributaries, *e.g.*, Washington Creek, Grassy Tributary, Twice Tried Tributary, and Burn Area Tributary, had pH values ranging from 6.6 to 7.5. These data indicate surface waters in the park are not susceptible to acidification from atmospheric deposition.

Mississippi NRRA

The 1995 *Baseline Water Quality Data Inventory and Analysis report* for Mississippi NRRA shows the large rivers, *i.e.*, the Mississippi, St. Croix, and Minnesota Rivers, are well-buffered, and so, are not susceptible to acidification. Minnehaha, Bassett, Rice, and Elm Creeks also appear to be well buffered, with pH values around 7.8. These data indicate acid deposition is not an issue in the park. However, some water samples showed elevated levels of nitrogen compounds, so eutrophication may be a concern. Given the urban nature of the park, it may be difficult to determine if the primary source of nitrogen input is airborne or waterborne. Some samples also showed elevated levels of metals like cadmium, copper, lead and mercury, as well as pesticides.

Pictured Rocks NL

The 1995 *Baseline Water Quality Data Inventory and Analysis report* for Pictured Rocks NL includes data from inland lakes, rivers and creeks. Lakes, such as Grand Sable, Kingston, Trappers, Beaver, Little Beaver, Chapel, Little Chapel, and Miners Lakes had average pH values from 6.8 to 7.9 and average ANC values from 160 to 1184 $\mu\text{eq/l}$. Hurricane, Mosquito, and Miners Rivers had average pH values from 6.3 to 7.9 and average ANC values from 336 to 768 $\mu\text{eq/l}$. Creeks, such as Sable, Grand Sable, Sullivan, Sevenmile, Beaver, Spray, and Chapel, had average pH values of 7.1 to 7.9 and average ANC values of 384 to 548 $\mu\text{eq/l}$. These data indicate surface waters in the park are not sensitive to acidification from atmospheric deposition. According to the report, no data have been collected in the park since 1984. Therefore, it is unclear if the 1995 report represents current conditions in the park.

Saint Croix NSR

The 1995 *Baseline Water Quality Data Inventory and Analysis report* for Saint Croix NSR indicates surface waters in the park are well-buffered against acidification, with pH values around 7.0 and ANC values of 500 $\mu\text{eq/l}$ or higher. Some samples showed elevated levels of heavy metals such as nickel, zinc, silver, and copper, but it may be difficult to determine if the primary source of these metals is airborne or waterborne.

Sleeping Bear Dunes NL

The 1997 *Baseline Water Quality Data Inventory and Analysis report* for Sleeping Bear Dunes NL includes data collected through 1995 from smaller lakes, rivers, creeks, and springs in the park, *e.g.*, Round, Loon, and North Bar Lakes, Crystal and Platte Rivers, Otter and Shelda Creeks, and Angell Springs. All had average pH values around 8.0, with no values lower than 6.5. Average ANC values ranged from 800 to 1200 µeq/l. These data indicate surface waters at Sleeping Bear Dunes NL are not sensitive to acidification.

Voyageurs NP

The 1995 *Baseline Water Quality Data Inventory and Analysis report* for Voyageurs NP includes data from a number of smaller lakes in the park such as Crane, Sandpoint, Lucille, Tooth, Ek, Cruiser, and Loiten. Lake pH values ranged from 6.0 to 7.4 and ANC values ranged from 116 to 216 µeq/l. These data indicate surface waters in the park are not sensitive to acidification from atmospheric deposition. According to the report, no data have been collected in the park since 1984. Therefore, it is unclear if the 1995 report represents current conditions in the park.

Air Toxics

Air toxics, *e.g.*, mercury, dioxins, and furans, may be a concern for all Great Lakes Network parks. A number of federal, state, local and private agencies, as well as Canadian agencies and universities, are conducting air toxics-related research and monitoring in the Great Lakes region. In addition, many organizations have been formed to coordinate monitoring efforts and disseminate information. Some of these organizations include the EPA Great Lakes National Program Office (<http://www.epa.gov/glnpo>); and the Great Lakes Commission, which among other things, is developing a web-based, searchable, environmental monitoring database for the Great Lakes basin (<http://www.glc.org>).

All four states with Network parks conduct air toxics monitoring as well as monitoring toxics in surface waters, sediments, and/or biota. All of the states measure mercury, at a minimum, in fish tissue for human consumption advisory programs, and mercury has been found in fish in all monitored waterways. According to EPA, all of the Great Lakes have fish with contaminant levels that are not safe for wildlife consumption. Management plans were developed for both Lake Michigan and Lake Superior in 2000. According to the Lake Superior Management Plan, 82 to 95 percent of polychlorinated biphenyls (PCBs) enter the lake through atmospheric deposition, 80 to 100 percent of dioxins are from atmospheric deposition, and 84 percent of mercury is from deposition. Critical pollutants in both lakes include PCBs, dieldrin, chlordane, DDT, mercury, dioxins and furans. Pollutants of concern are atrazene, arsenic, cadmium, chromium, copper, cyanide, lead, selenium, zinc, hexachlorobenzene, toxaphene, and polynuclear aromatic hydrocarbons (PAH).

Air Toxics Monitoring

Integrated Atmospheric Deposition Network

The Integrated Atmospheric Deposition Network (IADN) is a joint U.S.-Canada effort to monitor loading and trends of priority toxic chemicals to the Great Lakes and help determine the sources of those chemicals. The IADN has one Master Station on each of the five Great Lakes, supplemented by a number of Satellite Stations to provide more spatial detail. A complete range of measurements is made at the Master Stations, which involves measurement of wet and dry deposition of semivolatile organic compounds (including

PAHs, PCBs and organochlorines) and trace metals. A subset of measurements is made at Satellite Stations. Master Stations include Eagle Harbor, Michigan (Near Isle Royale NP) (initiated in 1990) and Sleeping Bear Dunes NL, Michigan (initiated in 1991). Satellite Stations include Chicago, Illinois (initiated in 1993); Turkey Lakes, Canada (initiated in 1994); and Sibley Provincial Park, Canada (initiated in 1993). Raw data and a list of publications are available on the program website; no data summary is provided (<http://www.epa.gov/glnpo/iadn>).

Mercury Deposition Network

The National Atmospheric Deposition Program has expanded its sampling to include the Mercury Deposition Network (MDN), which currently has over 80 sites. The MDN was formed in 1995 to collect weekly samples of precipitation, which are analyzed for total mercury. The objective of the MDN is to monitor the amount of mercury in precipitation on a regional basis (<http://nadp.sws.uiuc.edu/mdn>).

Current MDN sites in the Great Lakes region include: Indiana Dunes NL, Indiana (site #IN34) established in 2000; Belle Prairie, Minnesota (site #MN23 (Camp Riley)) established in 1996; Fernberg, Minnesota (site #MN18) established in 1995; Marcell Experimental Forest, Minnesota (site #MN16) established in 1995; Mille Lacs Lake Indian Reservation, Minnesota (site #MN22 (Mille Lacs Band of Ojibwe)) established in 2002; Brule River, Wisconsin (site #WI08) established in 1995; Devils Lake, Wisconsin (site #WI31) established in 2001; Middle Village, Wisconsin (site #WI32 (Neopit)) established in 2002; Popple River, Wisconsin (site #WI09) established in 1995; and Trout Lake, Wisconsin (site #WI36) established in 1995.

Trend analyses have not yet been performed for MDN sites. National wet mercury concentration and deposition maps show that values from monitors in the Great Lakes region are generally higher than those in the Northeast and Western U.S. and comparable to values in Florida and the Gulf Coast (see maps on MDN website).

National Dioxin Monitoring Network

The National Dioxin Monitoring Network (NDAMN) was established in 1998 to monitor the temporal and geographic variability of atmospheric dioxin at rural locations throughout the U.S. Sites in the Great Lakes region are located at Fond du Lac, Minnesota, and Dancy, Wisconsin. It doesn't appear that EPA has established a website for the program.

Indiana

As part of their regional air toxics monitoring program, ToxWatch, the Indiana Department of Environmental Management (IDEM) has been monitoring 87 chemicals at the Water Treatment Plant at Ogden Dunes, Porter County, since 1999 (<http://www.in.gov/idem/air>). At the Ogden Dunes site, concentrations of benzene, a known carcinogen, and chloromethane (methyl chloride), which affects the central nervous system, liver and kidneys, have both exceeded the cancer health benchmark levels recommended by EPA.

Michigan

The Michigan Department of Environmental Quality (MDEQ) published an air toxics monitoring strategy in June 2002. The strategy expands air toxics monitoring that's been ongoing since 1990. The proposed network will include an atmospheric deposition network to monitor persistent bioaccumulative toxics (PBT) and an ambient monitoring network to cover all other air toxics. The ambient network will consist of 35 sites and take five years to fully deploy. The network will monitor 35 volatile organic compounds, 13 carbonyl compounds, and 14 trace metals. A long-term background site will be located at Seney NWR (near Pictured Rocks NL), and a monitor to improve spatial coverage, which will operate for three or more years, will be located in Traverse City (near Sleeping Bear Dunes NL). The atmospheric deposition network will range from four to twelve sites and take three years to fully deploy. Monitored pollutants will include mercury, PCBs, dioxins, and furans. Monitoring would be added to the IADN sites at Eagle Harbor and Sleeping Bear Dunes NL, and a site would be installed at Sault Ste. Marie (http://www.michigan.gov/deq/0,1607,7-135-3310_4105---,00.html).

Minnesota

The Minnesota Pollution Control Agency (MPCA) has an extensive and long-term air toxics monitoring program. The MPCA monitors 75 air toxics at a number of locations throughout the state including Elk River (near Mississippi NRR), International Falls (near Voyageurs NP), Little Falls (near Mississippi NRR), Minneapolis-St. Paul (near Mississippi NRR and Saint Croix NSR), and Sandstone (near Saint Croix NSR). The highest concentrations of most pollutants are found at monitors in the Minneapolis-St. Paul area. The exception is ethylene bromide, which is found in higher concentrations in rural, rather than urban, areas.

Concentrations of formaldehyde, a respiratory irritant and probable carcinogen, have exceeded the inhalation health benchmarks at all sites. There has been no trend in formaldehyde concentrations since 1991. Maximum concentrations are measured in the summer, while lowest concentrations are measured in the winter. Mobile sources account for 58 percent of formaldehyde emissions, area sources emit 33 percent, and point sources account for 10 percent.

A small number of samples suggest concentrations of arsenic, a known carcinogen, exceed the benchmark at monitors in Elk River and Minneapolis-St. Paul. Ninety percent of arsenic emissions come from mining and iron ore processing.

Concentrations of benzene, a known carcinogen that affects the central nervous system, exceed the benchmark in Minneapolis-St. Paul. Concentrations have been decreasing over time. Sixty-six percent of benzene emissions are from mobile sources, 28 percent are from area sources, and 5 percent are from point sources.

Concentrations of carbon tetrachloride, a probable carcinogen that affects the central nervous system, kidneys, and liver, exceed the benchmark at all sites. Carbon tetrachloride was used as a refrigerator fluid and a propellant until the 1990s. Although it's no longer used, the pollutant is still found in air, water, and soil.

Concentrations of chloroform, a probable carcinogen that affects the central nervous system and liver, exceed the benchmark only at International Falls. There has been no trend in

chloroform concentrations at the site. The primary source of chloroform is pulp and paper mills.

Concentrations of ethylene dibromide, a probable carcinogen that affects the central nervous system, liver and kidneys, exceed the benchmark at monitors in International Falls, Little Falls and Sandstone. Ethylene dibromide is primarily used to scavenge lead out of aviation fuel and as a solvent. It contaminates groundwater and persists in soils. The reason for increased levels in rural areas is unknown (<http://www.pca.state.mn.us/air/index.html>).

Wisconsin

The Wisconsin Department of Natural Resources (DNR) monitored metals in ambient air at Superior from 1996 to 1999. It appears monitoring may have been discontinued in 1999 due to low levels (<http://www.dnr.state.wi.us/org/aw/air/MONITOR/AQMONITR.htm>).

Toxics Effects Monitoring

Indiana

The IDEM monitors water quality for a number of parameters; sediments and fish for concentrations of metals, persistent organic pollutants (POPs), and PCBs; and biotic integrity of macroinvertebrate and fish communities. Fish contaminant surveys are done on a 5-year rotation; the last survey in the Great Lakes was done in 2000. Fish and sediment contaminant concentrations have been monitored in the Calumet and Little Calumet Rivers. The IDEM does not operate any fixed-station water chemistry sites in Indiana Dunes NL (<http://www.in.gov/idem/water/programs>).

Minnesota

The MPCA is concerned about a number of PBTs that cannot be monitored in ambient air; but rather, require ecosystem or food web monitoring. The list of pollutants in this category comes from the Binational Toxic Strategy and the U.S. Great Lakes Water Quality Guidance. The list includes: dioxins (primarily emitted by waste incineration and pulp and paper mills), mercury (primarily point sources), PAHs (primarily from fuel combustion), PCBs (from insulation), hexachlorobenzene (many sources), cadmium (industrial uses and hazardous waste combustion), toxaphene (an insecticide), other chlorinated pesticides, and alkyl-lead. The MPCA monitors pollutant concentrations in water and sediments, and performs biotic integrity assessments of invertebrate and fish communities in lakes and rivers (for biotic integrity data contact Bob Murzyn at 651-296-6074 or Scott Niemela at 651-296-8878).

Because of particular concerns about mercury, the MPCA initiated the Mercury Contamination Reduction Initiative in 1999 which includes monitoring mercury concentrations as well as reducing mercury emissions. The MPCA reports that mercury emissions in the state dropped 68 percent between 1990 and 2000. Sediment cores taken from 50 lakes statewide, including 5 lakes in Voyageurs NP, were used to reconstruct the history of mercury deposition. The data show that, in some parts of the state (including the area around Voyageurs NP), mercury concentrations in core samples have declined by 15 to 20 percent since the 1970s. Fish tissue mercury concentrations are currently evaluated for 700 lakes for human consumption advisories (<http://www.pca.state.mn.us/air/mercury-mn.html>).

The USGS, in conjunction with the MPCA, has been coordinating a Long Term Resource Monitoring Program on the Upper Mississippi River System since 1987. Historical data are available at http://www.umesc.usgs.gov/data_library. The MPCA's Environmental Data Access Initiative for the Upper Mississippi River Basin will include expanded data collection and web-based access to chemical, physical and biological data from air, water, land and soils (<http://www.pca.state.mn.us/data/eda/index.html>).

Until recently the MPCA investigated frog deformities. Although no clear cause for the deformities has been identified, POPs, pesticides, and environmental estrogens have been suggested as potential causative agents. No frog deformities were reported to the MPCA near Grand Portage NM or Voyageurs NP; frog deformities have been reported in wetlands near Saint Croix NSR and Mississippi NRR (http://www.pca.state.mn.us/hot/frogs.html).

Wisconsin

The Wisconsin DNR has used lichens as air pollution biomonitors since 1991. They are currently using lichens to monitor regional ambient mercury levels in central Wisconsin (<http://www.dnr.state.wi.us/org/aw/air/MONITOR/bioweb/lichens.html>).

The DNR is monitoring contaminants in sediments and fish tissues near Ashland. While current monitoring does not encompass sites near Apostle Islands NL, this summer the state will expand its fish sampling program (contact John Robinson at 715-365-8976 for further information).

Park Studies

Much of the following information was obtained from the NPS Investigators Annual Report (IAR) database for each park.

Apostle Islands NL

Amphibian surveys were conducted in 1998 and 1999. Two malformations and 58 cases of asymmetry were observed (Gary Casper, 414-278-2766, affiliation unknown).

Lichens were collected for elemental analysis in 2001 and 2002 to compare against earlier records. Concentrations of some elements increased while others decreased (Cliff Wetmore, 612-625-6292, University of Minnesota).

Mercury concentrations will be determined for hair samples collected from American otters on Apostle Islands NL (Thomas Doolittle, 715-682-7123, Bad River Natural Resources).

Grand Portage NM

Lichens were collected for elemental analysis in 1993. Results were not provided on the IAR website (Cliff Wetmore, 612-625-6292, University of Minnesota).

Indiana Dunes NL

The International Joint Commission recognizes the south shore of Lake Michigan as one of 43 Principle Areas of Concern (AOC) due to all the industry in the area. Accordingly, park-sponsored studies have included water chemistry sampling and evaluation of contaminant loads in aquatic invertebrates, plants and animals (Richard Whitman, 219-926-8336x424, USGS).

From 1997 to 2000, brown bullhead catfish, channel catfish and bluegill sunfish were evaluated as biomonitors for the effects of environmental carcinogens in aquatic environments of the Great Lakes region. Study results were not provided on the IAR website (Ron Gregg, 765-494-3607, Purdue University).

From 1995 to 2001, sediments were collected for contaminant analysis and aquatic toxicity tests. High levels of contaminants were found at some sites. Toxicity testing is currently underway (Paul Stewart, Indiana Dunes NL).

Heavy metals, nutrients, and pH levels were measured in foliage samples, leaf litter, and within each of the three soil horizons at a number of sites in the park in 2000 through 2002. Chemical analyses of nearly all of the elements sampled in soils demonstrated a decreasing gradient from west to east, as did pH. This pattern was most evident in the two transects nearest the lake shore. Soil organic matter did not vary significantly along the transects. The spatial pattern of chemical elements in plant shoots and roots was less clear (Jim Bennett, 608-262-5489, USGS).

A 2002 study of accumulation rates of heavy metals (*i.e.*, Cd, Cr, Cu, Mn, Pb, and Zn) retained in wetland sediments in Northwest Indiana assessed human influences on atmospheric deposition rates over the last 100 years. The wetland sites lie downwind of the Chicago-Gary-Hammond industrial complex, historically one of the most industrialized regions of the U.S. Results showed accumulation rates for the last 100 years have increased by factors of 5 (Cd) to 30 (Zn); remaining effectively constant for Cr. Accumulation at the flooded sites is 1.6 - 1.7 times greater than at the drained site for all metals except Zn, which is about 4 times greater. The results suggest that over the historic period the flooded wetlands have retained most atmospheric inputs of heavy metals (Catherine Souch, 317-274-1103, Indiana University).

Isle Royale NP

Lichen surveys in 1992 found elevated sulfur concentrations in lichens collected near Thunder Bay, Ontario, relative to lichens collected at other locations in the park (Jim Bennett, 608-262-5489, USGS).

In the summer of 1998, sediment cores were collected from Lake Siskiwit to determine whether or not the concentrations of selected atmospherically-deposited semivolatile compounds have been decreasing in recent years. Comparison of these time trends from Lake Siskiwit with a sediment core from Lake Superior would allow the PIs to investigate whether changes in a lake representing primarily atmospheric deposition differ from one that has many possible point source inputs. Results were not provided on the IAR website (Ron Hites, 812-855-0193, University of Indiana).

Toxaphene concentrations and seasonality were determined in samples of water, phytoplankton, zooplankton, mysis, diporeia and fish from Lake Superior and Siskiwit Lake in 1998 and 1999. Results were not provided on the IAR website (David De Vault, 612-713-5340, U.S. Fish and Wildlife Service).

An inland lake survey found northern pike with mercury concentrations that exceeded the fish consumption advisory levels. A follow-up study is focusing on Sargent Lake (high fish mercury levels) and Richie Lake (lower fish mercury levels) and looking at mercury in sediments, water, plankton, and fish. The initial study also looked at mercury concentrations in deer mice collected in the Sargent Lake watershed and in moose teeth collected throughout the island. Data suggest mercury is more bioavailable to zooplankton in Sargent Lake, and differences in mercury accumulation between the lakes are due to within-lake processes rather than differences in atmospheric input (James Hurley, 608-262-3979 and David Armstrong, 608-262-0768, both at University of Wisconsin).

As a consequence of finding high mercury concentrations in lake water, in 1998 through 2001, researchers investigated concentrations of mercury in lichens and soil samples collected throughout the island. The soil scientists found that geologically-derived mercury in the park is very low, and concluded that the predominant cause of soil mercury is atmospheric deposition. Mercury concentrations showed a gradient, with higher concentrations in the upper soil layers. Overall, mercury concentrations were higher at the northeast end of the park and were higher near lakes with high mercury concentrations (Bill Cannon, 703-648-6345, and Laurel Woodruff, 763-783-3291, both of USGS).

In summer 2002, three sediment cores were collected from Siskiwit Lake and analyzed for concentrations of polybrominated diphenyl ethers (PBDEs) and PCBs. The cores from the park are assumed to provide background levels of contaminants for a Great Lakes-wide study (An Li, 312-996-9597, University of Illinois).

Pictured Rocks NL

Lichens were collected for elemental analysis in 1992 and 1993. Results were not provided on the IAR website (Jim Bennett, 608-262-5489, USGS).

Saint Croix NSR

In 1995, the NPS and the USGS entered into an Interagency Agreement to enhance water quality and ecological sampling and analysis in areas where National Parks and National Water-Quality Assessment (NAWQA) studies coexist. The NAWQA project is being conducted by a team of hydrologists, biologists, chemists, and hydrologic technicians. Water quality and ecological field work in 1995 consisted of a reconnaissance survey, water quality sampling of the St. Croix River near Danbury, Wisconsin and bed sediment and tissue sampling at four sites on the Namekagon and St Croix Rivers. Endosulfan-I, an insecticide, was the only compound detected and was detected at all three sites (near Danbury, near Sunrise and at Hudson). Fish, invertebrates, and algae were collected during 1996 and 1997 at three sites in the St. Croix NSR: Namekagon River near Leonards, St. Croix River near Danbury, and the St. Croix River near St. Croix Falls. During 1998, fish were collected at all three sites listed above; however, algae and invertebrate samples were collected only at the St. Croix River near Danbury. In addition to ecological data collection, the physical habitat was characterized, hydrologic measurements were made, and water chemistry samples were collected at each site. In 1999, fish and invertebrate community composition, and nutrient, organic carbon, suspended sediment, and major ion concentrations were measured or collected at 14 sites along the mainstem of the St. Croix River from Danbury to Hudson. Increased concentrations or loads downstream of a particular tributary or population center will

give an indication of impaired reaches that may require additional routine monitoring or more detailed study (Kathy Lee, 763-783-3254, USGS).

In 2000 and 2001, mercury and methylmercury concentrations were characterized at 17 tributary stream sites in the St. Croix River Basin during summer low-flow (base flow) conditions. Tributaries in the St. Croix River Basin were identified that deliver disproportionately high levels of methylmercury, relative to other Basin tributaries. Potential correlations between mercury (methylmercury and total mercury) and landscape features, such as percent of watershed covered in wetlands, cropland, and forested area were determined. Seasonal and hydrologic variations in mercury and methylmercury concentrations in the water column at the Namekagon River at Leonards, Wisconsin, were assessed. Results were not provided on the IAR website (Greg Payne, 763-783-3233, USGS).

Sleeping Bear Dunes NL

Lichens were collected for elemental analysis in 2000 to compare against earlier records. Concentrations of some elements increased while some decreased (Cliff Wetmore, 612-625-6292, University of Minnesota).

Voyageurs NP

Based on a study conducted from 1988 to 1992, the PI concluded that bald eagle reproduction at Voyageurs NP was impaired due to organochlorine contamination. In 1999 to 2000, the PI did a follow up study and collected blood and feather samples from 16 nestling eagles. He found that concentrations of PCBs, DDE, and mercury had declined from the earlier sampling period (Bill Bowerman, 864-646-2185, Clemson University).

From 1993 to 1997, U.S. Fish and Wildlife Service and NPS staff also investigated the role of environmental contaminants in eagle reproductive success at the park. Results showed eaglet mercury concentrations, but not total PCBs or DDE, differed among the four major lakes within the park. However, no significant correlations between eaglet tissue PCBs, DDE, or total mercury and mean 5-year productivity were observed (Keren Giovengo, 410-573-4538, U.S. Fish and Wildlife Service).

A 1993 through 1995 study investigated mercury contaminant levels and potential reproductive effects in red-necked grebes, common mergansers and hooded mergansers nesting in Voyageurs NP. Results were not provided on the IAR website (Mary Derr, 612-624-3785, University of Minnesota).

In 1997, breeding common loons were monitored for reproductive success and mercury concentration in blood and feather samples. Mercury concentrations were provided, but no discussion was provided as to whether or not the levels were high (Cory Counard, 612-624-3785, University of Minnesota).

An ongoing study initiated in 2000 is investigating the distribution of mercury in rocks and soils in small watersheds within the park and looking for possible contributions of mercury from terrestrial environments to aquatic environments. Preliminary data examination indicates that most of the mercury found in soils of the park is from an

atmospheric source rather than from bedrock or glacial material (the PI indicates the same is probably true for lead and sulfur). As a result, highest mercury levels are found in organic-rich A-horizon soils where mercury is strongly bound to organic carbon. The mercury in this organic layer can be easily volatilized during a fire, leading to high mercury concentrations in smoke (Laurel Woodruff, 763-783-3291, USGS).

An ongoing study is investigating the seasonality and annual mean concentrations of total mercury and methylmercury in 18 to 20 lakes in Voyageurs NP and examining relationships of aqueous mercury species to selected water chemistry data (major ions, pH, alkalinity, organic carbon); to landscape features (soil cover, soil mercury levels, percentage of watershed that is forested or covered in wetlands, etc.); and to fish-mercury levels, in study lakes (Robert Goldstein, 763-783-6375, USGS).

A study initiated in 2002 is determining total and methylmercury concentrations in crayfish from several small lakes in the park. Results will indicate their contribution to mercury levels in predators such as otters (Michael Sydor, 218-726-7205, University of Minnesota).

A three year project, initiated in 2002, will determine if emissions of contaminants, specifically PAHs from recreational snowmobile use in Voyageurs NP, pose a potential hazard to the quality of the aquatic ecosystems in the park. The project involves collecting and analyzing sediment samples from aquatic systems in snowmobile use and non-use areas to assess the potential for PAH residues to move into aquatic systems within the park, deployment of semipermeable membrane device (SPMD) integrative samplers to assess the presence of waterborne bioavailable PAH residues, and onsite toxicity testing using an invertebrate test species and water from the aquatic systems in both the snowmobile use and non-use areas. The first phase (2002/2003) involved collecting sediment samples. The second phase (2004) of the research will involve deploying SPMDs in the two aquatic systems and conducting the onsite toxicity testing (Jim Petty, 573-876-1824, USGS).

Particulate Matter

Small or “fine” particles in the air, typically those less than 2.5 microns in diameter, PM_{2.5}, are a leading cause of human respiratory illness. Particles are present everywhere, but high concentrations and/or specific types have been found to present a serious danger to human health. Fine particles in the air are the main contributor to human-caused visibility impairment. The particles not only decrease the distance one can see; they also reduce the colors and clarity of scenic vistas. Moisture in the air enhances the impact, so areas in the Eastern U.S., with higher relative humidity, have worse visibility than areas in the arid West (see attached visibility maps).

The current human-health based National Ambient Air Quality Standards (NAAQS) for particulate matter (set by the EPA) are for particles 10 microns or less (PM₁₀). Areas where air quality exceeds the NAAQS for PM₁₀ are designated “nonattainment” for that pollutant. There are no areas in Indiana, Michigan, Minnesota, and Wisconsin currently designated nonattainment for PM₁₀.

In 1997, EPA finalized new stricter NAAQS for particulate matter based on PM_{2.5}. Nationwide PM_{2.5} monitoring was initiated in 1999; nonattainment areas will not be designated until 2004. Preliminary data shows that the Chicago/Southeast Wisconsin/Northwest Indiana area will likely be designated nonattainment for PM_{2.5}, including Porter County, Indiana where Indiana Dunes NL is located.

Visibility

In 1985, in response to the mandates of the Clean Air Act, Federal and regional/state organizations established the Interagency Monitoring of Protected Visual Environments (IMPROVE) program to protect visibility in Class I air quality areas (<http://vista.cira.colostate.edu/improve>). Class I areas are national parks greater than 5,000 acres and wilderness areas greater than 6,000 acres, that were established prior to August 7, 1977. All other NPS areas are designated Class II. In the Great Lakes area, Voyageurs NP and Isle Royale NP are Class I areas. The objectives of the IMPROVE program are: to establish current visibility conditions in all Class I areas; to identify pollutants (particles and gases) and emission sources responsible for existing man-made visibility impairment; and to document long-term trends in visibility. In 1999, there were 30 official IMPROVE sites and 40 protocol sites. Because of recently enacted regulations that require improving visibility in Class I areas, the number of visibility monitors is increasing. Protocol sites are being upgraded to full IMPROVE sites and 80 new sites are being added to the IMPROVE network.

While the IMPROVE program has focused on Class I air quality areas, a great deal of visibility monitoring has been conducted in Class II areas. The ARD recommends that new visibility monitoring in NPS areas be conducted in coordination with the IMPROVE program (the IMPROVE program is managed out of the NPS ARD office in Fort Collins, Colorado). Some I&M Networks are considering monitoring visibility at scenic vistas with digital cameras. While this type of monitoring would not be adequate for regulatory purposes, it is useful for documenting visibility conditions and trends and provides an excellent means of sharing that information with the public. Cameras are currently located at Seney NWR, Michigan, and Grand Portage Indian Reservation, Minnesota (<http://www.mwhazecam.net>).

The following IMPROVE sites are located in the Great Lakes region: Bondville, Illinois (site #BOND) established in 2001; Isle Royale NP, Michigan (site #ISRO) established in 1999 (previous site operated 1988 to 1991); Seney NWR, Michigan (site #SENE) established in 1999; Boundary Waters Canoe Area, Minnesota (site #BOWA) established in 1991; and Voyageurs NP, Minnesota (site #VOYA) established in 1999 (previous site operated 1988 to 1996). An IMPROVE site is also planned for Great River Bluffs, Minnesota (site #GRRI). (See attached table for nearest monitors to Great Lakes parks.) Long-term visibility trends have not yet been determined for any IMPROVE sites in the Great Lakes region. As for the sources of visibility impairment, 1996 to 1998 aerosol data from Boundary Waters Canoe Area show that, on an annual basis, visibility impairment is primarily due to sulfates (sources include coal combustion and oil refineries), then organics (sources include automobiles and chemical manufacturing), then nitrates (sources include coal and natural gas combustion and automobiles), then soil (from windblown dust), and then light absorbing carbon (sources include wood burning). Contributions from nitrates and organics are almost equal from November through

March, but the contribution from organics is much higher than that from nitrates the rest of the year. At the site, visibility is best in the winter and worst in the summer.

Ozone

Ozone is created by a chemical reaction between oxides of nitrogen (NO_x) and volatile organic compounds (VOC) in the presence of heat and sunlight. Some major sources of ozone-forming chemicals are motor vehicle exhaust and industrial emissions, gasoline vapors, and chemical solvents.

High ozone concentrations cause respiratory problems in humans, and are a particular concern for those who are engaging in strenuous aerobic activity, such as hiking. Ozone also damages sensitive plant species. It injures plant leaves by causing a visible spotting or “stipple” on the upper surface of the leaves. Ozone can affect plant physiology by reducing growth, increasing susceptibility to disease, and increasing senescence.

Ambient Monitoring

The EPA sets NAAQS for ozone based on human health effects. The current ozone NAAQS is based on a 1-hr concentration of 0.12 parts per million (ppm). If this threshold is exceeded on more than one day per year (on a 3 year average), the area is considered “nonattainment” for the 1-hr ozone standard. Current 1-hr ozone nonattainment areas include Lake and Porter County, Indiana, (Indiana Dunes NL) and eight Wisconsin counties along Lake Michigan.

EPA recently established a new NAAQS for ozone, which is based on a 3-year average of the 4th highest daily maximum 8-hr ozone concentration. This value cannot exceed 0.08 ppm, or the area will be designated nonattainment. Nonattainment areas for the new ozone NAAQS will be designated in 2004.

An EPA analysis of ambient monitoring data from 1998-2000 shows that the 8 Wisconsin counties along Lake Michigan from Door County to the Illinois state line are exceeding the 8-hr ozone standard, as are all Illinois and Indiana counties along Lake Michigan (including Indiana Dunes NL). Several Michigan counties along the west shore of Lake Michigan are also exceeding the 8-hr ozone standard, including Benzie County where the southern portion of Sleeping Bear Dunes NL is located.

The following is based on a review of monitored ozone values from 2000-2002, unless otherwise stated:

Apostle Islands NL

The nearest ozone monitor is located in Boulder Junction, Vilas County, Wisconsin, 70 miles southeast. The average maximum 8-hr ozone concentration at this monitor is 0.73 ppm. The average 4th high 8-hr concentration is 0.068 ppm. Ozone concentrations at this monitor increased from 1991–1999 but have been falling since.

Another monitor is located in Carleton County Minnesota, 80 miles southwest. The average maximum 8-hr ozone concentration (2001-2002) at this monitor is 0.071 ppm. The average 4th high 8-hr concentration (2001-2002) is 0.058 ppm. This site has only been operating since 2001, so there are not enough data to show trends.

Grand Portage NM

The nearest ozone monitor is on Isle Royale, 20 miles east of Grand Portage NM. This monitor began operating in 2002. The highest 8-hr concentration in 2002 was 0.066 ppm. There is not enough data at this monitor to show trends.

Another ozone monitor is located in the Boundary Waters Canoe Area, 60 miles west. The average maximum 8-hr ozone concentration at this monitor is 0.075 ppm. The average 4th high 8-hr concentration is 0.063 ppm. Ozone concentrations at this monitor have remained fairly steady over the past 10 years.

Indiana Dunes NL

The average maximum 8-hr ozone concentration at this monitor is 0.102 ppm. The average 4th high 8-hr concentration is 0.083 ppm. Other nearby monitors show even higher concentrations, exceeding the NAAQS for 8-hr ozone. There is not a discernable trend in ozone concentrations at this site.

Isle Royale NP

There is a new ozone monitor on Isle Royale. This monitor began operating in 2002. The highest 8-hr concentration in 2002 was 0.066 ppm. There is not enough data at this monitor to show trends

The Boundary Waters Canoe Area monitor discussed above under Grand Portage NM is located about 80 miles west of Isle Royale NP

Mississippi NRR

There are several ozone monitor sites near the Mississippi NRR. Readings are fairly consistent among the monitors, with maximum 8-hr concentrations of about 0.085 ppm and 4th-high concentrations of about 0.071 ppm. These monitors don't show any significant trends.

Pictured Rocks NL

An ozone monitor site at Seney NWR, in the Upper Peninsula of Michigan (about 25 miles southeast of Pictured Rocks NL), began collecting data in 2002. The maximum 8-hr ozone concentration measured in 2002 was 0.091 ppm. The 4th high reading was 0.083 ppm. This site is too new to show trends.

Saint Croix NSR

The nearest ozone monitor is located in Stillwater, Minnesota, 3 miles west of the river. The average maximum 8-hr ozone concentration at this monitor is 0.086 ppm. The average 4th high 8-hr concentration is 0.073 ppm. There is no discernible trend in concentrations at this monitor.

Sleeping Bear Dunes NL

The nearest ozone monitor site is located in Benzie County, Michigan, about 5 miles south. The average maximum 8-hr ozone concentration at this monitor is 0.106 ppm. The average 4th high 8-hr concentration is 0.086 ppm. This value exceeds the NAAQS. Ozone concentrations at this site increased from the early 1990s, but don't show a trend in recent years.

Voyageurs NP

An ozone monitor site is located at Voyageurs NP. The average maximum 8-hr ozone concentration at this monitor is 0.071 ppm. The average 4th high 8-hr concentration is 0.064 ppm. Concentrations at this monitor have been dropping slightly since it began operating in 1996.

Vegetation

To determine if Great Lakes Network parks have ozone-sensitive plant species, park vascular plant lists contained in the NPSpecies database (January 2003) were compared to the lists of Ozone-Sensitive Plant Species compiled for the NPS ARD (see attached species lists). The Ozone-Sensitive Plant Species lists were developed by an expert in the field of ozone effects on vegetation. Note that the lists provide a general guide to ozone sensitivity. Differences in plant genetics, weather conditions, soil water availability, and ozone concentrations will affect whether or not a species exhibits injury in a park. In particular, studies have shown that plants will not take up ozone unless there is sufficient soil moisture. Ozone sensitive species of natural vegetation were identified for all nine Network parks (see attached lists of sensitive species for Network parks).

It is generally agreed that plant foliar injury occurs after a cumulative exposure to ozone. One ozone metric that is used to evaluate the risk of plant injury is SUM06. SUM06 is the sum of all hourly average ozone concentrations greater than or equal to 0.06 ppm. In 1997, a group of ozone effects experts recommended 3-month, 8:00 a.m. to 8:00 p.m., SUM06 effects endpoints for natural vegetation, *i.e.*, 8 to 12 ppm-hrs for foliar injury to natural ecosystems and 10 to 15 ppm-hrs for growth effects on tree seedlings in natural forest stands.

According to the SUM06 map generated for the Air Inventory (attached), Indiana Dunes NL, Pictured Rocks NL, and Sleeping Bear Dunes NL may have SUM06 ozone concentrations high enough to harm native vegetation (16-34 ppm-hrs, 11-15 ppm-hrs, and 16-20 ppm-hrs, respectively). The ARD has contracted with a plant physiologist to evaluate historic ozone concentration and soil moisture data to assess the likelihood of finding ozone-induced foliar injury in I&M parks and to develop standardized protocols for ozone injury surveys. The risk assessment should be completed for the Great Lakes Network by June 2003, and the protocols should be available in early 2004.

The states of Indiana, Michigan, Minnesota, and Wisconsin, in cooperation with the U.S.D.A. Forest Service, have been conducting foliar injury surveys for ozone for a number of years. Species examined include blackberry (*Rubus* spp), black cherry (*Prunus serotina*), common milkweed (*Asclepias syriaca*), yellow poplar (*Liriodendron tulipifera*), white ash (*Fraxinus americana*), sassafras (*Sassafras albidum*), sweetgum (*Liquidambar styraciflua*), pin cherry (*Prunus pensylvanica*), spreading dogbane (*Apocynum androsaemifolium*), and big leaf aster (*Aster macrophyllus*). A minimum of 10 and a maximum of 30 plants of each species are evaluated. Plants are evaluated in mid-August. From 1997 to 2001, injury was observed in survey plots in Indiana Dunes NL and near Saint Croix NSR in Wisconsin. Injured species at Indiana Dunes NL included milkweed (3 of 30 stems in 2000 and 5 of 30 stems in 2001) and black cherry (1 of 10 branches in 2001). Injury has also been observed in plots near Apostle Island NL

and Sleeping Bear Dunes NL. The severity of injury, *i.e.*, number of plants and leaves injured, and amount of injury per leave, has been very light in most plots (<http://www.fiaozone.net>).

Conclusions

The NPS is concerned about the ambient concentrations and potential effects of a number of air pollutants in units of the National Park System. The pollutants and effects of primary emphasis are: 1) fine particles and their effects on human health and visibility, 2) ozone and its effects on human health and vegetation, and 3) sulfur and nitrogen deposition and their effects on soils, surface waters, and biota. In some areas, including the Great Lakes region, air toxics are also of concern.

It is always desirable to collect ambient air quality data on-site, particularly if air pollution sensitive resources have been documented in a park. However, the high cost of monitoring precludes the NPS from monitoring ambient air quality in every park. Ideally, off-site data can be used to indicate pollutant concentrations at a park. A number of factors, *e.g.*, differences in elevation and meteorology, location of pollution sources, and urban versus rural settings, influence how well an off-site monitor represents pollutant concentrations in a park.

Ambient air quality in Great Lakes Network parks appears to be generally well monitored. The attached table lists, by park, the distance to the nearest wet deposition, dry deposition, IMPROVE, and ozone monitors.

All the Great Lakes Network parks have NADP/NTN (wet deposition) sites within 35 miles. With the exception of Voyageurs NP, which has a CASTNet (dry deposition) site, parks are between 45 and 165 miles from the nearest CASTNet site. This distance between parks and CASTNet monitoring is not unusual given the small number of CASTNet monitors across the country. The relative abundance of wet deposition monitors is probably appropriate since the bulk of the deposition in this area (~85% at Voyageurs NP) is in the form of wet deposition.

Most Great Lakes Network parks have ozone monitors within 25 miles. Apostle Islands NL is the exception with the nearest ozone monitor 70 miles away. Portable ozone monitors and passive monitors are two alternatives to expensive continuous ozone monitors. While these alternatives will not provide data that can be used for regulatory purposes, they can give an idea of ozone concentrations and trends. Portable monitors collect data that are comprehensive enough to evaluate the ozone threat to vegetation.

As discussed earlier, IMPROVE monitors are generally located to measure visibility in "Class I" air quality areas. Thus, the Class I parks (Voyageurs and Isle Royale) have on-site monitors. For other Great Lakes parks, proximity to an IMPROVE monitor largely depends on how close the park is to a Class I park or another Class I area (such as the Boundary Waters Canoe Area Wilderness or the Seney NWR). Class II parks' distances from IMPROVE monitors range from 25-140 miles.

As mentioned above, it is also possible to monitor visibility at scenic vistas with digital cameras. While this type of monitoring would not be adequate for regulatory purposes, it

is useful for documenting visibility conditions and trends and provides an excellent means of sharing that information with the public. Cameras are currently located at Seney NWR, Michigan, and Grand Portage Indian Reservation, Minnesota (<http://www.mwhazecam.net>).

While a good bit of ambient air toxics monitoring has been and is being conducted in the Great Lakes area, these efforts do not seem to be well-coordinated on a regionwide basis, and the data from the various monitoring programs are not readily available. The Network may want to consider having the existing data consolidated and analyzed to help determine if more ambient air toxics and/or toxics effects monitoring is warranted.

Air toxics may be an issue for many Great Lakes Network parks. A great deal of toxics effects monitoring and research has been conducted at Indiana Dunes NL, Isle Royale NP, Mississippi NRR, Saint Croix NSR, and Voyageurs NP. It is possible that USGS- and state-sponsored programs provide adequate monitoring at Mississippi NRR and Saint Croix NSR. Network staff may want to determine if there are any critical park areas that are not encompassed by those monitoring programs. For good reason, monitoring at Isle Royale NP and Voyageurs NP has focused on mercury and its effects. Network staff should determine if there are other air toxics that should be considered for an effects monitoring program (e.g., chloroform at Voyageurs NP?). Very little, or no, air toxics effects monitoring has been conducted at Apostle Islands NL, Grand Portage NM, Pictured Rocks NL, or Sleeping Bear Dunes NL. Network staff should consider performing some synoptic sampling in these parks to evaluate the need for long-term toxics effects monitoring.

Park water quality data were reviewed for all nine Great Lakes Network parks. The data indicated surface waters at Apostle Islands NL (e.g., at Oak Island, Outer Island, and Stockton Island) are sensitive to acidification from atmospheric deposition. Network staff may want to consider long-term monitoring of acid deposition-related water chemistry parameters, such as pH and ANC, at the park. Nitrogen-associated eutrophication may be a concern for Indiana Dunes NL and Mississippi NRR.

Ozone sensitive vascular plant species have been identified for all of the parks in the Great Lakes Network. Ozone concentrations may be high enough in three parks, *i.e.*, Indiana Dunes NL, Pictured Rocks NL, and Sleeping Bear Dunes NL, that foliar injury surveys are warranted. An ARD-funded risk assessment that will be completed for Great Lakes Network parks in June 2003 will provide further guidance on the likelihood of ozone-induced vegetation damage in Network parks.

Relevant Websites

NPS Air Inventory (*Air Atlas*) - <http://www2.nature.nps.gov/ard/gas>

NADP - <http://nadp.sws.uiuc.edu>

CASTNet - <http://www.epa.gov/castnet>

IADN - <http://www.epa.gov/glnpo/iadn>

MDN - <http://nadp.sws.uiuc.edu/mdn>

Indiana DEM - <http://www.in.gov/idem>

Michigan DEQ - <http://www.michigan.gov/deq>

Minnesota PCA - <http://www.pca.state.mn.us>

Wisconsin DNR - <http://www.dnr.state.wi.us>

IMPROVE - <http://vista.cira.colostate.edu/improve>

Ozone (and other) Air Monitor Data - <http://www.epa.gov/air/data/index.html>

Ozone Injury - <http://www.fiaozone.net>